Indian J. Phys. **78(12)**, 1377-1380 (2004)

AN INTERNATIONAL JOURNAL
IJP

Overtone spectra of phenol derivatives

Garima Tripathi, Vineet Kumar Rai and S B Rai*

Laser and Spectroscopy Laboratory, Department of Physics, Banaras Hindu University, Varanasi-221 005, Uttar Pradesh, India

E-mail : sbrai49@yahoo.co.in

Received 21 April 2004, accepted 16 September 2004

Abstract : Overtone spectra of 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol have been analyzed in the 2500–14000 cm^{-1}region. The vibrational frequencies and the anharmonicity constants for the C-H and O-H stretching vibrations have been evaluated. The effect of the substitution of chlorine atom at different positions of the phenol ring has been studied. The observations are well supported by theoretical calculations for the charge density and the bond lengths using molecular orbital AM1 method. The possibility of intramolecular hydrogen bonding involving O-H-Cl has also been marked in the case of 2-chlorophenol and 2,4-dichlorophenol. It is noted that in the case of 4-chlorophenol, the shift in C-H stretching frequency is proportional to the sum of the Hammett (σ) of the substituents while in the case of 2-chlorophenol it is only 55% of the value in 4-chlorophenol.

Keywords : Overtone spectra, phenol derivatives, vibrational constants.

PACS Nos. : 33.15.Mt, 39.30.+w

1. Introduction

As is well known, the study of highly excited vibrational levels in the ground electronic state of polyatomic molecules provides valuable information about the dissociation of the molecule, nonradiative energy transfer, effect of substitution on the vibrational frequency, inter- and intra-molecular hydrogen bonding *etc*. Studies of NH, OH and CH stretching vibrations are important since the frequencies are large enough and these play a dominant role in such processes. Recently, we [1,2] have reported the vibrational overtone spectra of aniline and its chloro as well as its aliphatic derivatives. In the case of halo-derivatives, it is marked that C-H/N-H stretching vibrations are appreciably affected due to the presence of electron withdrawing/electron donating substituent. However, in the case of o-chloroaniline, it is found that NH stretch-frequency remains unchanged as compared to that of aniline due to the formation of intra-molecular hydrogen bond between H atom of NH_2 group and chlorine atom.

Mizugai and Katayama [3–5] have studied the overtone spectra of large number of benzene derivatives and have reported the changes in the frequencies of the CH vibrational modes. It is noted that the shift in the case of p-disubstituted benzenes is approximately equal to sum of the frequency shifts in the corresponding monosubstituted benzenes. Yadav and Singh [6] have reported the intermolecular hydrogen bonding in CCl_4 diluted o- and m-ethyl phenols. They found that the broad bands due to associated OH peak at ~3450 cm^{-1} and ~3340 cm^{-1} disappear at very low concentrations (~0.05%) and sharp bands appear at 3620 cm^{-1} and at 3630 cm^{-1} respectively for two isomers.

The OH stretching vibration in phenol-$(H_2O)_n$ (n = 1, 2, 3) complexes have been investigated by IR-UV double resonance spectroscopy [7]. It is seen that in the phenol-H_2O complex, the ν_{OH} band is observed at 3524 cm^{-1}, at a red shift of ~133 cm^{-1} from that of free phenol, the shift is attributed to hydrogen bonding between phenol and the water clusters.

Recently, Pandit and Chudasama [8] have studied the IR spectrum of p-chlorophenol. They have reported the characteristic free OH stretch band to lie in the 3600 cm^{-1} region and C-H stretching fundamentals near 3086 cm^{-1}. Several other weak bands, either due to overtone or combination bands, are also reported.

*Corresponding Author

Mizugai and Katayama [9] have detected the fifth overtone of the aryl C-H stretching vibration in phenol and found that the frequency shift from the corresponding band of benzene is proportional to σ_I values of the substituents.

In this paper, we have recorded the IR and NIR spectra of 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol. The bands involving Δv = 1,2,3 and 4 for CH/OH stretching vibration for all these molecules have been monitored and these data have been used to determine the vibrational frequencies, anharmonicity constants and dissociation energies for the CH and the OH stretch vibrations using local mode model. We have also made a molecular orbital calculation using AM1 model to estimate the charge density on the C, O and H atoms in the presence and absence of chlorine at different positions of the ring in phenol and also estimated the bond length. It is seen that our measurements are in consonance with the theoretical calculations.

2. Experimental

The samples of 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol obtained from BDH, India with 99.9% purity and 2,6-dichlorophenol and 2,4,6-trichlorophenol obtained from Merck with 99% purity, were used in the present study without any further purification.

The IR spectra were recorded using a JASCO-FTIR-5300 model while for NIR spectra, a Lambda-19-UV-Vis-NIR double beam spectrophotometer was utilized. For each measurement, the cuvette was well cleaned and rinsed before filling the sample for final measurements. All these measurements were made at room temperature (25°C) with sample path length of 1 cm. Several scans were made for each measurement. For higher harmonics, the peaks appear with very small intensity. The positions of the peaks were ascertained by increasing the sensitivity in the reported scans.

3. Result and discussion

The absorption spectra of the five molecules recorded in the 2500–14000 cm^{-1} region. The IR spectra of these compounds show three peaks in 3100 cm^{-1} region due to various C-H stretching vibrations and a broad peak due to OH stretching vibration in 3500 cm^{-1} region. The NIR spectrum is for 2-chlorophenol shown in Figure 1. The peaks near 6050 cm^{-1} region and 6900 cm^{-1} regions are due to second harmonics of C-H and O-H stretching

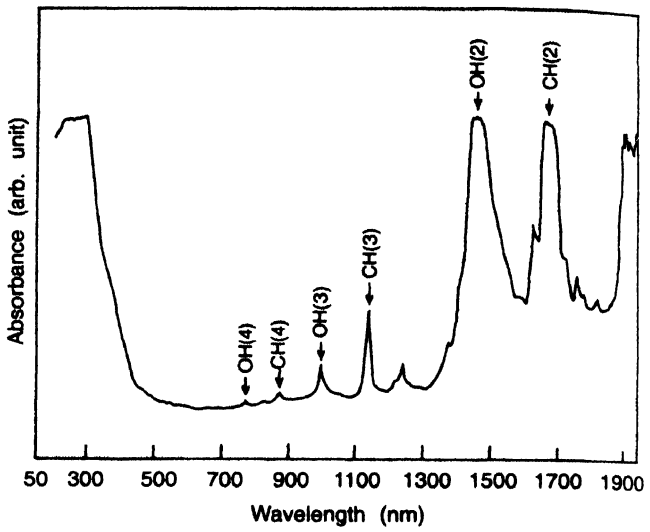

Figure 1. NIR spectra of 2-chlorophenol.

vibrations respectively. There also appear some weak peaks in the 5100–5900 cm^{-1} region and these are due to combination bands of CH/OH stretching vibrations and their deformation modes. The third harmonics of these stretching vibrations appear in 8850–10000 cm^{-1} regions. Along with these harmonics peaks, some weak peaks are also observed in the 7100–8500 cm^{-1} region, which are due to combination modes. In all these compounds the intensity of the peak decreases as we move towards the higher harmonics, while the bandwidth of the bands increases rapidly. The Δv = 4 bands C-H and O-H stretching vibrations appear with very weak intensity. The vibrational frequencies of the bands along with their FWHM for all the five molecules are given in Table 1.

The vibrational frequencies and the anharmonicity constants for the two stretching vibrations were calculated using the relation given by Ellis [10],

$$\Delta E_v = Av + Bv^2 \qquad (1)$$

where A and B are constants related with vibrational frequency ($\omega_e = A-B$) and anharmonicity ($-\omega_e x_e = B$). v refers the quantum number of the excited vibrational levels and ΔE_v the transition energy for (v, 0) band. The vibrational constants for CH and OH stretching vibrations for all the five molecules thus obtained along with their estimated error are given in Table 2. The dissociation energies for these molecules are also given in the same Table 2.

A. Overtone bands due to C-H stretching vibration :

The vibrational frequencies and the anharmonicity constants for all the five molecules are compared in Table 2. From the table it is clear that the C-H stretching frequency for

Table 1. Fundamental and overtone transitions frequencies (in cm^{-1}) for CH/OH stretching vibrations in 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, and 2,4,6-trichlorophenol.

Molecule	$\Delta v = 1$	$\Delta v = 2$	$\Delta v = 3$	$\Delta v = 4$
2-Chlorophenol				
CH stretch	3060	6009.6	8810	11494.2
	(20)	(126)	(147)	(-)
OH stretch	3493	6826	10000	12987
	(40)	(200)	(370)	(-)
4-Chlorophenol				
CH stretch	3064	5988	8772	11428
	(19)	(133)	(222)	(-)
OH stretch	3540	6920	10131.3	13195.2
	(35)	(136)	(350)	(-)
2,4-Dichlorophenol				
CH stretch	3080	6056	8917	11640
	(10)	(76)	(96)	(-)
OH stretch	3504	6930	10132	13146
	(35)	(52)	(86)	(-)
2,6-Dichlorophenol				
CH stretch	3090	6037	8870	11572
	(30)	(86)	(101)	(-)
OH stretch	3538	6912	10101	13120
	(25)	(77)	(91)	(-)
2,4,6-Trichlorophenol				
CH stretch	3100	6036	8872	11540
	(12)	(62)	(164)	(-)
OH stretch	3536	6908	10091	13092
	(25)	(51)	(130)	(-)

(-) FWHM values

Table 2. Molecular constants and error estimated for CH and OH stretching vibration in 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, and 2,4,6-trichlorophenol.

Molecule	A (cm^{-1})	$-B = \omega_e X_e$ (cm^{-1})	$A-B = \omega_e$ (cm^{-1})	$D_e = \omega_e^2/4\omega_e X_e$ (eV)
2-Chlorophenol				
CH stretch	3129.8 ± 5.0	64.1 ± 1.4	3193.8 ± 6.4	4.9 ± 0.3
OH stretch	3580.7 ± 4.2	83.3 ± 1.2	3663.9 ± 5.4	4.9 ± 0.2
4-Chlorophenol				
CH stretch	3131 ± 2.1	68.5 ± 0.6	3199.5 ± 0.7	4.6 ± 0.1
OH stretch	3620 ± 4.3	80.0 ± 1.3	3700 ± 5.6	5.3 ± 0.1
2,4-Dichlorophenol				
CH stretch	3145.7 ± 4.9	58.7 ± 1.4	3204.4 ± 6.4	5.4 ± 0.4
OH stretch	3624.2 ± 18.9	83.8 ± 5.5	3707.9 ± 24	5.1 ± 0.2
2,6-Dichlorophenol				
CH stretch	3148.3 ± 3.1	63.8 ± 0.9	3212.2 ± 3.9	5.0 ± 0.2
OH stretch	3628.7 ± 2.1	87.2 ± 0.5	3715.9 ± 2.5	4.9 ± 0.1
2,4,6-Trichlorophenol				
CH stretch	3161.8 ± 6.9	69.1 ± 0.2	3230.5 ± 8.9	4.68 ± 0.4
OH stretch	3631.6 ± 3.2	89.5 ± 0.9	3721.4 ± 4.1	4.8 ± 0.04

2,4,6-trichlorophenol is the largest as compared to the C-H stretching vibrational frequency of other molecules (including benzene and phenol). This is due to electron withdrawing character of the chlorine atom. In 2,4,6-trichlorophenol there are three chlorine atoms attached with the ring these chlorine atoms withdraw the electronic charge from the ring and reduce the electronic charge density on the ring carbon atoms. Due to this reduction in the charge density on carbon atoms of the ring, the bond length between the ring carbon atoms and the adjacent hydrogen atom attached, decreases. Therefore, the force constant as well as the vibrational frequency increases. In the case of 2-chlorophenol and, 4-chlorophenol, the change in the C-H stretching vibrational frequency is small as compared to that of phenol 2,4-dichlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol. In the case of 2-chlorophenol and 2,4-dichlorophenol, there exists intra-molecular hydrogen bonding between the chlorine atom attached with the ring at ortho-position and the H atom of OH group. Again the C-H stretching vibrational frequency of 2,4-dichlorophenol is greater than that of 2-chlorophenol. The presence of two chlorine atoms, one at ortho and other at para position, add to the charge redistribution causing this increase. In 2,6-dichlorophenol and 2,4,6-trichlorophenol, intra-molecular hydrogen bonding is ruled out, because the two chlorine atoms at the second and the sixth positions of the ring cancel the hydrogen bonding. The shift in the CH stretching vibrational frequency from that of benzene in 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol are 47 cm^{-1}, 52 cm^{-1}, 57 cm^{-1}, 65 cm^{-1} and 83 cm^{-1} respectively, which clearly shows the increasing effect of chlorine substitution at the different position of the ring in phenol. Of course, the shift is not linearly proportional to the total number of chlorine atoms. In order to verify the change in vibrational frequency due to the presence of chlorine atom at different positions in phenol, we calculated the charge density at different atoms in phenol compounds using AM1 molecular orbital method (see Table 3). From Table 3, it is clear that the excess charge density at the ring carbon atom follows the trend 2,4,6-trichlorophenol < 2,6-dichlorophenol < 2,4-dichlorophenol < 4-chlorophenol < 2-chlorophenol. Therefore, the change in the C-H stretching vibrational frequency follows a reverse order. In this case, it is pointed out that for 4-chlorophenol where there is least interaction between hydroxyl group with chlorine, the shift in C-H stretching frequency for $\Delta v = 3$ is proportional

Table 3. Excess charge density at the position of carbon atom of the benzene ring and at oxygen atom of the OH group.

Molecule	Charge density on carbon atom	Charge density on 'O' atom of the OH group
Phenol	–0.0970	–0.2526
2-Chlorophenol	–0.0938	–0.2369
4-Chlorophenol	–0.0901	–0.2482
2,4-Dichlorophenol	–0.0896	–0.2331
2,6-Dichlorophenol	–0.0838	–0.2299
2,4,6-Trichlorophenol	–0.0797	–0.2263

to sum of the Hammett σ of the substituent (*i.e.* sum of Hammett σ for Cl). While in the case of 2-chlorophenol, it is only 55% of the 4-chlorophenol. This change is due to the hydrogen bonding between H atom of OH and Cl atom. We have also calculated the C-H bond length (ν_{CH}) in these molecules by using the relation given by [5],

$$\nu_{CH} = 1.084 - \{8 \times 10^{-5} \times \Delta\nu/\nu\} \quad (2)$$

where 1.084 A° is the bond length of the C-H bond in benzene, $\Delta\nu$ is the frequency shift and ν is the vibrational quantum number. The values thus obtained from eq. (2) are listed in Table 4.

Table 4. C-H bond length for 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,6- dichlorophenol, and 2,4,6-trichlorophenol.

Molecule	Bond length (A°)
Phenol	1.0837
2-Chlorophenol	1.0835
4-Chlorophenol	1.0832
2,4-Dichlorophenol	1.0819
2,6-Dichlorophenol	1.0811
2,4,6-Trichlorophenol	1.0803

B. Overtone bands due to O-H stretching vibration :

Bands involving $\Delta\nu$ =1, 2, 3 and 4 transitions for O-H stretching vibration are seen for all the five molecules. It is noted that these bands are very broad, the intensities of which decrease as we move towards the higher harmonics. From Table 2, it is clear that vibrational frequency for OH band for these molecule follows the trend : 2,4,6-trichlorophenol > 2,6-dichlorophenol > 2,4-dichlorophenol > 4-chlorophenol > 2-chlorophenol. It is marked that the OH stretching vibrational frequency for 2-chlorophenol and 2,4-dichlorophenol are nearly same as that of phenol. The reason is that in this case, there exists intra-molecular hydrogen bonding between H atom of OH group and Cl atom attached at the ortho position of the ring. But the existence of excess charge on chlorine atom at para position in 2,4-dichlorophenol, reduces the charge density on the 'O' atom of the OH group, therefore the OH stretching vibrational frequency in this case, is greater than that of 2-chlorophenol. Substitution of chlorine atom at different position of the ring not only affects the charge density on the ring carbon atom, but it also affects the charge density on 'O' atom of the OH group. In the case of 4-chlorophenol, 2,6-dichlorophenol and 2,4-dichlorophenol, the formation of intramolecular hydrogen bonding is ruled out by the geometry.

Acknowledgment

Authors are grateful to the Department of Science and Technology, Govt. of India for financial assistance.

References

[1] Vineet Kumar Rai, S B Rai and D K Rai *Spectrochim. Acta* A59 1299 (2003)

[2] Vineet Kumar Rai, Amareswar Rai, D K Rai and S B Rai *Spectrochim. Acta* **A60** 53 (2004)

[3] Y Mizugai and M Katayama *Bull. Chem. Soc. Jpn.* **53** 2081 (1980)

[4] Y Mizugai, M Katayama and N Nakagawa *J. Am. Chem. Soc.* 103 5061 (1981)

[5] Y Mizugai and M Katayama *Chem. Phys. Lett.* **73** 240 (1980)

[6] R A Yadav and I S Singh *Indian J. Pure Appl. Phys.* **23** 626 (1985)

[7] S Tanabe, T Ebata, M Fujii and N Mikami *Chem. Phys. Lett.* 215 347 (1993)

[8] B Pandit and U Chudasama *Bull. Mater. Sci.* **24** 265 (2001)

[9] Y Mizugai and M Katayama *J. Am. Chem. Soc.* **102** 6424 (1980)

[10] J W Ellis *Trans. Faraday Soc.* **25** 265 (1947)